

**SPECIFICATION****METHOD FOR MEASURING TEMPERATURE USING MINUTE SIZE  
TEMPERATURE SENSING ELEMENT****Technical Field**

The present invention relates to a temperature measuring method using a minute size temperature sensing element. More specifically, it relates to a novel temperature measuring method capable of measuring the temperature accurately in a wide range, using a temperature sensing element comprising a carbon nanotube containing a columnar gallium.

**Background Art**

After the discovery of the carbon nanotube in 1991, a number of studies have ever been carried out by many researchers. Then, various technical improvement and utilization methods have been found out concerning the carbon nanotube. For example, nowadays, it is utilized widely for the field effect devices, the probe top ends for the scanning probe microscopes, the superconductive materials, the highly sensitive microbalances, the structural materials, the minute forceps for the nanoscale operation, the parts for the gas detector, the hydrogen energy storage devices, or the like. Moreover, the studies have been executed actively for containing the various fillers in the carbon nanotube (Document 1 and Document 2).

For example, as the substances to be contained in the carbon nanotube, a metal such as a lead, a tin, a copper, an indium and a mercury, an alkali metal such as a lithium, a sodium, a potassium, a rubidium, and a cesium, a superconductor such as a lead, a tin, and a gallium, a semiconductor such as a silicon, a germanium, a gallium arsenide, a zinc selenide, and a zinc sulfide, a magnetic material such as a samarium, a gadolinium, a

lanthanum, an iron, a cobalt and a nickel, and a mixture thereof have been discussed.

Moreover, an organic molecule semiconductor such as a naphthalene, an anthracene, a phenanthrene, a pyrene, and a perylene, an organic dye molecule such as a cyanine dye and a  $\beta$ -carotene, and furthermore, a gas molecule such as a hydrogen fluoride, a methane, and an ethane, or the like have been discussed.

On the other hand, recently, a number of researchers have been involved in the study field of the micrometer size area so that the nano thermometer capable of measuring the temperature in the micrometer size environment has been more and more called for. However, the nano thermometers known so far have a relatively narrow measurable temperature range so that several kinds of the thermometers need to be prepared for each temperature range to be measured in the case of measuring the temperature in a wide range. Due to the troublesomeness and the high cost, development of the nano thermometer capable of measuring the temperature in a wide range by itself has strongly been desired.

Under such circumstances, a nano thermometer utilizing a gallium, capable of accurately measuring the temperature in a relatively wide temperature range has been proposed. As the principle of the temperature measurement, the linear expansion or contraction of the gallium according to the temperature change in a wide range is utilized. By measuring the change of the length of the columnar gallium by a high resolution transmission electron microscopy, the temperature is measured.

Then, the production method for a temperature sensing element comprising a carbon nano tube having a 1 to 10  $\mu\text{m}$  length for containing the columnar gallium and a 40 to 150 nm diameter is known already (Document 3). Moreover, by the present inventors, the production method for a temperature sensing element according to the heat treatment at 1,200 to 1,400°C of gallium oxide powders and carbon powders under the inert gas flow has been developed and it is already filed for the patent application (Application 1).

However, as to the temperature measuring method, utilizing a nano thermometer

utilizing a gallium discussed so far, the length of the columnar gallium as the temperature sensing element cannot be read out unless the subject to be measured is introduced into the observation area of the high resolution transmission type electron microscope. On the other hand, once the temperature sensing element is taken out from the inside of the subject to the outside for the temperature measurement, since the length of the columnar gallium returns to the length at the room temperature, the accurate temperature of the subject at the high temperature cannot be known.

Document 1: P. Ajayan et al., Nature, vol. 361, page 333, 1993

Document 2: Official gazette of the Japanese Patent Application Laid Open No. 6-227806

Document 3: Gao, Y.H. & Bando Y., Nature, 415,599 (2002)

Application 1: Patent Application No. 2002-67661

Accordingly, an object of the present invention is to solve the above-mentioned problems by providing a novel method capable of accurately measuring the temperature of a subject to be measured at a high temperature even in the case a columnar gallium temperature sensing element as a nano thermometer utilizing a gallium is taken out from the inside of the subject to have the temperature measured for the measurement at the room temperature.

#### **Disclosure of Invention**

In order to solve the above-mentioned problems, the present invention provides a method for measuring the temperature using a minute size temperature sensing element, as a temperature sensing element comprising a carbon nano tube with a continuous columnar gallium contained with one end opened and the other end closed, characterized in comprising the steps of measuring the gallium length by a transmission electron microscopy in different temperature environments, inserting the temperature sensing element into a subject to be measured in the air, and taking out the temperature sensing

element from the subject to be measured for measuring the gallium length by the transmission electron microscopy.

#### **Brief Description of Drawings**

**FIG. 1** is a high resolution transmission electron microscope image of a gallium-containing carbon nano tube temperature sensing element before heating, observed at 20°C.

**FIG. 2(A)** is a high resolution transmission electron microscope image of the gallium-containing carbon nano tube temperature sensing element after heating to 358°C in the air, observed at 20°C, and **FIG. 2(B)** is a graph of an energy dispersive X-ray spectroscopy thereof.

**FIG. 3** is a high resolution transmission electron microscope image of the gallium-containing carbon nano tube temperature sensing element at 440°C in the air.

**FIG. 4** is a high resolution transmission electron microscope image of the gallium-containing carbon nano tube temperature sensing element after heating to 440°C in the air, observed at 20°C.

The numeral in the figures denotes the following.

1. gallium oxide thin layer

#### **Best Mode for Carrying Out the Invention**

The present invention has the above-mentioned characteristics. The embodiments thereof will be explained hereinafter.

According to the temperature measuring method of the present invention, first, a temperature sensing element comprising a carbon nano tube with one end opened and the other end closed, containing a continuous columnar gallium is introduced into the observation area of a high resolution transmission electron microscope maintained at different temperatures for measuring the length of the gallium at each temperature.

Then, the temperature sensing element is inserted into a subject to have the temperature measured so as to be placed in a heated environment in the air atmosphere. According to the heating operation, the volume of the gallium is expanded as well as the top end part thereof is oxidized so as to produce a gallium oxide. Since the gallium oxide is bonded with the carbon nano tube firmly so that the gallium oxide at the top end part has its position fixed even when the temperature sensing element is taken out from the subject to be measured, the temperature sensing element is taken out from the subject to have the temperature measured after cooling for measuring the length of the gallium of the temperature sensing element again using the high resolution transmission electron microscope. Thereby, the temperature of the subject to have the temperature measured can be measured.

Accordingly, the nano thermometer of the present invention utilizes the expansion characteristics of the gallium present inside the carbon nano tube according to the temperature change so that in principle it is not different from a thermometer used in general for measuring the expansion or contraction change of a mercury.

However, it differs therefrom in that the carbon nano tube has about a 1 to 10  $\mu\text{m}$  length and a 40 to 150 nm diameter for the measurement of the temperature in a micrometer size environment so that it is extremely minute compared with the thermometer used in general. Therefore, in order to measure the length of the gallium in the minute carbon nano tube, use of an optical instrument such as a high resolution transmission electron microscope is necessary.

According to the present invention, as the reason for selecting the gallium as the substance to be contained in the carbon nano tube, the gallium as the widest liquid phase range (29.78 to 2,403  $^{\circ}\text{C}$ ) among the metals so that it has the excellent characteristics of a low vapor pressure at a high temperature. Furthermore, since the gallium has the volume increased linearly according to the temperature rise in a 50 to 500 $^{\circ}\text{C}$  temperature range, and furthermore, it has the volume reduced linearly in the case of lowering the

temperature, it is suitable as a thermometer required to measure the temperature in a wide temperature range.

For example, compared with the liquid phase range (-38.87 to 356.58°C) of a mercury used for an ordinary temperature, it has a wide temperature measurement range at a high temperature range, and thus the effect of using the gallium for the nano thermometer is apparent.

As to the carbon nano tube containing a gallium, it can be produced according to various kinds of methods including a known method explained as the conventional technique, a method proposed by the present inventors, et al..

Then, with reference to the examples, embodiments will be explained in further details.

## **Examples**

### **<Example 1>**

A temperature sensing element was produced according to the method disclosed in the above-mentioned document 3. The structure thereof was confirmed by a high resolution transmission electron microscopy with an X-ray energy diffusion spectrometer mounted. The temperature sensing element was applied onto a grid for the observation by the high resolution transmission electron microscopy. Then, the temperature sensing element was observed by the high resolution transmission electron microscopy maintained at 20°C and 58°C for measuring the height of the gallium.

FIG. 1 is a high resolution transmission electron microscope image showing the height of the gallium at the time of observing the temperature sensing element at 20°C. FIG. 2(A) is an image of the temperature sensing element observed again at 20°C using the high resolution transmission electron microscope after introducing the same into a furnace in the air, heating at 358°C and taking out. As shown in FIG. 2(A), the top end position of the gallium is made higher than the top end position of the gallium in FIG. 1.

Accordingly, the gallium position is made higher despite the measurements at the same ordinary temperature 20°C because the gallium top end part is reacted with an oxygen so as to produce a gallium oxide, and the produced gallium oxide is firmly bonded with the inner wall of the carbon nano tube so that the gallium oxide layer position at the high temperature is not lowered even after the temperature drop.

This can be confirmed also by the inclusion of the oxygen at the gallium top end part as observed in the energy dispersive X-ray spectroscopy shown in FIG. 2(B).

#### <Example 2>

FIG. 3 is an image of the same temperature sensing element as the example 1 observed using the high resolution transmission electron microscope after heating to 440°C. FIG. 4 is an image thereof observed at 20°C using the same high resolution transmission electron microscope after heating and taking out.

From FIG. 4, since the gallium oxide layer is bonded firmly with the inner wall of the carbon nano tube, the gallium oxide thin layer position is not changed even after the temperature drop.

It is confirmed that gallium layer (1) of a low density layer is formed in the lower part of the gallium layer, and that the gallium oxide layer is bonded firmly with the inner wall of the carbon nano tube.

As a result of the measurement using the high resolution transmission type electron microscope accordingly, the height difference of the gallium top ends in FIG. 1 and FIG. 2(A) was 170 nm. According to the calculation using the numerical values, the gallium volume  $V_0$  initially at 20°C was  $9.586 \times 10^7 \text{ nm}^3$ , the increased volume  $\Delta V_1$  at the time of heating to 58°C was  $2.333 \times 10^5 \text{ nm}^3$  ( $\Delta V_1/V_0 = 0.24\%$ ), and the volume increase amount  $\Delta V_2$  at  $T_h$ °C was  $2.577 \times 10^6 \text{ nm}^3$ . By substituting these values in the formula  $T_h = 58 + \Delta V_2/a_0 (V_0 + \Delta V_1)$ , (wherein  $a_0$  is the expansion coefficient of the gallium at 58°C [ $0.95 \times 10^{-4}/^\circ\text{C}$ ]),  $T_h = 341^\circ\text{C}$  can be obtained as the calculation value.

Although the value is slightly lower than the real measurement value 358°C, it

was confirmed that the temperature can be measured considerably accurately at a high temperature.

As to the difference of the calculation value and the real measurement value, it is considered that the gallium volume  $V_0$  calculated with the premise that the carbon nano tube inner diameter is increased linearly is larger than the real gallium volume, the gallium density is lowered due to the oxygen diffusion, or the like.

#### **Industrial Applicability**

According to the present invention, the temperature measurement of the micrometer size environment can be enabled, and furthermore, the temperature measurement in a wide temperature range of 50 to 500°C can be enabled.